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14. ABSTRACT The dissociative recombination of $\text{OPCl}^+$ and $\text{OPCl}_2^+$ has been studied at the storage ring CRYRING. The rate constants as a function of electron temperature have been derived to be $7.63 \times 10^{-7} (T_e/300)^{-0.89}$ and $>1/2 \times 10^{-6} (T_e/300)^{-1.22} \text{ cm}^3 \text{ s}^{-1}$ , respectively. The lower limit quoted for the latter rate constant reflects the experimental inability to detect all of the reaction products. The branching fractions from the reaction have been measured for $\text{OPCl}^+$ at $\approx 0 \text{ eV}$ interaction energy and are determined to be $N(\text{O}+\text{P}+\text{Cl})=(16\pm 7)$ , $N(\text{O}+\text{PCl})=(16\pm 3)\%$ and $N(\text{OP}+\text{Cl})=(68\pm 5)\%$ . These values have been obtained assuming that the rearrangement channel forming $\text{P}+\text{ClO}$ is negligible, and <i>ab initio</i> calculations using GAUSSIAN03 are presented for the ion structures and energetic to support such an assumption. Finally, the limitations to using heavy ion storage rings such as CRYRING for studies into the dissociative recombination of large singly charged molecular ions are discussed.					
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# Dissociative recombination of $\text{OPCl}^+$ and $\text{OPCl}_2^+$ : Pushing the upper mass limit at CRYRING

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The dissociative recombination of  $\text{OPCl}^+$  and  $\text{OPCl}_2^+$  has been studied at the storage ring CRYRING. The rate constants as a function of electron temperature have been derived to be  $7.63 \times 10^{-7} (T_e/300)^{-0.89}$  and  $> 1.2 \times 10^{-6} (T_e/300)^{-1.22} \text{ cm}^3 \text{ s}^{-1}$ , respectively. The lower limit quoted for the latter rate constant reflects the experimental inability to detect all of the reaction products. The branching fractions from the reaction have been measured for  $\text{OPCl}^+$  at  $\approx 0 \text{ eV}$  interaction energy and are determined to be  $N(\text{O}+\text{P}+\text{Cl})=(16 \pm 7)\%$ ,  $N(\text{O}+\text{PCl})=(16 \pm 3)\%$  and  $N(\text{OP}+\text{Cl})=(68 \pm 5)\%$ . These values have been obtained assuming that the rearrangement channel forming  $\text{P}+\text{ClO}$  is negligible, and *ab initio* calculations using GAUSSIAN03 are presented for the ion structures and energetics to support such an assumption. Finally, the limitations to using heavy ion storage rings such as CRYRING for studies into the dissociative recombination of large singly charged molecular ions are discussed. © 2008 American Institute of Physics.  
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## I. INTRODUCTION

Much recent environmental debate has focused on the role that motor vehicles play in everyday life, ranging from the use of biofuels and electric cars to the efficiency of fuel-air combustion engines. Several aspects related to the latter of these areas have been to look at ways of making the fuel itself cleaner, e.g., by including additives which can either control or effect the amount of environmentally sensitive chemicals released from the combustion process—in the same way that a catalytic converter cleans up the exhaust—or to increase the efficiency of the combustion process, which would then have the knock on effect that the energy output from the process could be maintained but that less fuel is consumed. Ion-molecule chemistry has been shown to increase the rate of hydrocarbon combustion when ions are present in the combustion environment<sup>1–4</sup> while oxyphosphorus compounds have been shown to be effective replacements for phosphine fuel additives.<sup>5</sup> Consequently, several studies on the ion-molecule chemistry of phosphorus oxychloride compounds have been done using flow tube instruments in order to understand the transition from the primary electron attachment products of  $\text{OPCl}_3$  to the stable, fully oxygenated anion species,  $\text{PO}_3^-$  and  $\text{PO}_2^-$  (Refs.6–10). These two ions have been observed in the flame environment to be the primary terminal ions.<sup>11,12</sup>

One of the possible competing reactions for removing electrons from the plasma is dissociative recombination (DR). DR involves the attachment of a typically low energy ( $< 1 \text{ eV}$ ) electron to a singly charged molecular ion which then dissociates into neutral fragments. Indeed, DR has also

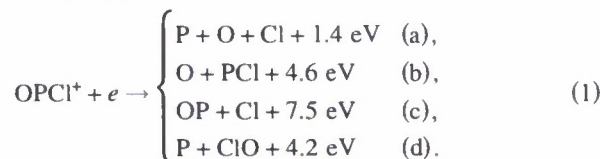
been suggested as a possible reaction process that increases the efficiency of combustion engines since it leads to the production of reactive radical species which can then react further.<sup>13</sup> Several techniques have traditionally been used to measure the DR reaction rate, as well as the products that arise from the reaction, from flow tube instruments to merged beams experiments. One extension of the latter technique, which has proven to be especially successful in the study of DR, has been the heavy ion storage ring since it combines the ability to measure to high precision both the reaction rate constant and the reaction products with the same experimental setup, something which is not usually possible in flow tube instruments. Over the last ten years a considerable body of data, i.e., cross sections, rate constants, and reaction products has been generated from DR experiments at both storage rings and flow tube instruments, and several reviews of these data and comparisons between data sets have recently been published.<sup>14–16</sup>

In spite of the uniqueness of the information, the current generation of ion storage rings has several limitations, including the ability to conduct experiments at only 300 K and, of relevance to DR, for only relatively low mass singly charged molecular ions. The former places some constraints on the asymptotic internal temperature of the ions, especially if their internal modes couple effectively with the 300 K black-body radiation. The latter arises from the requirement to velocity match the ion and electron beams for  $\approx 0 \text{ eV}$  collisions, which is experimentally determined by the ability to create and confine a sufficiently dense electron beam to allow the reaction to proceed. In CRYRING, the ion energy in the laboratory frame is given by  $96q^2/M$ , where  $q$  and  $M$  are the charge state and mass of the ion, respectively. For a

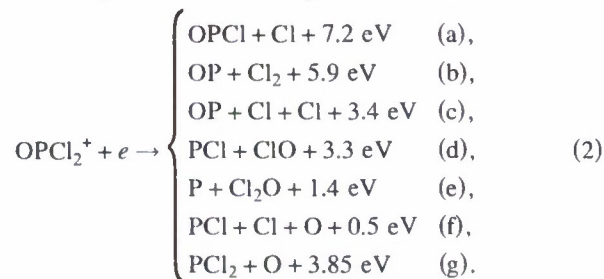
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singly charged molecular ion with mass of 96, this corresponds to 1 MeV total beam energy and gives rise to an electron beam of only 5.7 eV. The low kinetic energy of the ions also places constraints on the unique identification of the reaction products. The detectors used in storage rings to determine the products from the DR reaction are ion-implanted silicon detectors which essentially convert the kinetic energy given up by the particles in the active volume of the detector—through the creation of electron-hole pairs—to a proportional output voltage. The resolution is determined by the electrical noise generated in the crystal, and if the noise is the same order as the signals arising from real particles, then unique identification of the reaction products becomes difficult. Some solutions to this problem have been suggested, but their range of applicability is limited, and these are also discussed in the recent review articles.<sup>14–16</sup>

The present study addresses both of the issues raised above: an investigation into the DR of heavy singly charged phosphorus oxychloride compounds of relevance to combustion additives, e.g.,  $\text{OPCl}^+$  and  $\text{OPCl}_2^+$ . The DR of  $\text{OPCl}^+$  at 0 eV interaction energy can proceed through four available reaction channels



It is noted that channel (1d) involves the recombination of the two “outside” atoms as determined from the structure calculations which are discussed later. In the DR of  $\text{OPCl}_2^+$ , the following channels are energetically available:



The exothermicity of these reaction channels [Eqs. (1) and (2)] has been determined using both Ref. 17 and the calculations presented later in this paper. Due to the relatively high mass of the ions, some difficulties have been encountered putting constraints on the measurement of both the reaction rate constant and the reaction products, i.e., it has not been feasible to measure the complicated branching fractions in the DR reaction of  $\text{OPCl}_2^+$ .

## II. EXPERIMENT AND *AB INITIO* CALCULATIONS

The measurements were made at the CRYRING facility located at Stockholm University. The apparatus has been described in detail previously<sup>18</sup> and so only the salient details which are relevant to the present measurements will be mentioned here. Both  $\text{OPCl}^+$  and  $\text{OPCl}_2^+$  were created from  $\text{OPCl}_3$  in a hot filament ion source. In order to save the liquid and the filament from the corrosive nature of  $\text{OPCl}_3$ , the

vapor was pulsed into the source in conjunction with the injection cycle. In doing so, the high concentration of  $\text{OPCl}_3$  necessary for the production of a usable amount of ions was only present in the source for short periods of time. The ion of choice was mass selected, injected into the ring, and accelerated to the maximum allowed energy. The isotopologue  $\text{OP}^{37}\text{Cl}^+$  was used since it gives a slightly better mass resolution when determining the reaction products. Furthermore,  $\text{OP}^{37}\text{Cl}^+$  is isobaric with  $^{84}\text{Kr}^+$  and since it is easy to create large ion currents with the latter ion this simplified the setting up of the experimental ring parameters, i.e., the ion beam transport and storage in the ring, and made switching to  $\text{OPCl}^+$  relatively easy in spite of the relatively low flux. Since product determination was impossible for the heavier species, the dominant isotopologue  $\text{OP}^{35}\text{Cl}_2^+$  was used. Once in the ring, the ions were subjected to the normal measurement cycle including a period in which the ion beam was cooled in the electron cooler.<sup>19</sup> Electron cooling implies a reduction of the phase-space occupied by the ions through their interaction with the cold electron beam characterized by longitudinal and transverse energy spreads of 0.1 and 2 meV, respectively. Under the cooling conditions, the electron and ion beams have the same velocity, i.e., have a relative collision energy close to 0 eV. However, due to the heavy nature of the ions, the cooling period was not long enough to ensure that the ions reached the same energy spread as the electrons. As such, the main purpose of the electron cooler in the present experiment was only to serve as an electron target. However, both ions have nonzero dipole moments and the cooling period was sufficient for spontaneous photon emission leading to vibronically ground state ions. The electron cooler cathode voltage was tuned away from the cooling conditions which enabled us to vary the relative collision energy. The cathode voltage was ramped in such a way that the electrons were initially faster than the ions and then their relative velocity decreased until they were slower. As such, the relative collision energy varied from 1 eV through 0 to 1 eV again. Monitoring the count rate of the DR products  $dN/dt$  as a function of the cathode voltage, the energy-dependent cross section was calculated as

$$\sigma(E) = \frac{1}{v_{\text{rel}}} \frac{dN}{dt} \frac{v_e v_i e^2 \pi r_e^2}{I_e I_i l}, \quad (3)$$

where  $v_{\text{rel}}$  is the relative velocity between electrons and ions,  $v_e$  and  $v_i$  are the electron and ion velocities in the laboratory frame, respectively,  $I_e$  and  $I_i$  are the electron and ion currents, respectively,  $e$  is the elementary charge,  $r_e$  is the electron beam radius, and  $l$  is the length of the electron cooler. The obtained result was corrected for the toroidal regions of the electron cooler and space-charge effects induced by the electrons.<sup>20,21</sup>

The heavy nature of the ions, at 84 and 117 amu, results in the relatively low kinetic energies of the beams, 1.12 and 0.8 MeV, respectively. This led to several experimental difficulties, e.g., due to the insufficient electron cooling, the ion beam profiles were quite broad which could lead to products from the DR process missing the detector. A DR event appears in the pulse-height spectrum at the total beam energy unless one or more of the fragments miss the detector. In the

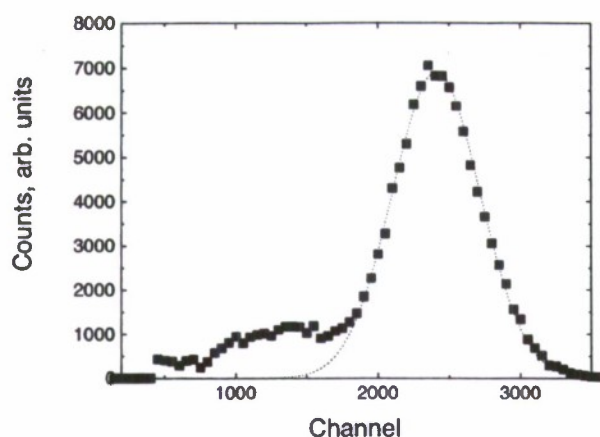


FIG. 1. Background-subtracted pulse-height spectrum for the DR reaction of  $\text{OPCl}^+$  recorded at  $\approx 0$  eV interaction energy is shown by solid squares. The dotted curve presents the Gaussian fit to the full beam energy peak.

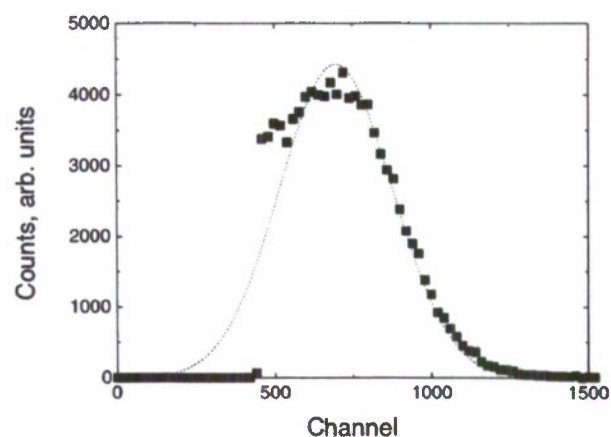


FIG. 2. The solid squares show background-subtracted pulse-height spectrum for the DR reaction of  $\text{OPCl}_2^+$  recorded at  $\approx 0$  eV interaction energy. The dotted curve presents Gaussian fit to the total mass peak. The abrupt cutoff is due to the electrical noise becoming comparable to the DR signals.

latter case, the energy is reduced by the percentage of total mass which is lost. In the pulse-height spectrum recorded for the DR reaction of  $\text{OPCl}^+$  (Fig. 1), the presence of the lower energy signals implies that losses were occurring and the contribution of these losses to the total data was calculated to be 16%. A Gaussian best fit to the total energy peak (Fig. 1) would represent a pulse-height spectrum in the ideal case when all particles are detected. For cross section measurements, the loss of particles is easily corrected for since it is purely a multiplicative factor. In the case of the heavier  $\text{OPCl}_2^+$  ion, which has an even lower kinetic energy, the measurements of both the reaction rate constant and the reaction products were even more experimentally complicated, since the fragment loss issue was much more substantial than for  $\text{OPCl}^+$  and could not be accounted for in the analysis. In order to extract some information, a detector with larger geometrical size was used. This enabled the particle losses to be essentially suppressed, though, on the other hand, this led to significantly worse energy resolution due to the increased contribution from the electrical noise generated in the detector. A Gaussian fitting procedure revealed that some of the fragments were still missed (Fig. 2), though to a much lesser extent than with the smaller detector. Moreover, counts in the loss channels were dominated by the detector noise making it

impossible to quantify the amount of loss. Therefore, the cross section measurements represent a lower limit to the real values.

Branching fractions were obtained by inserting a grid in front of the detector with a transmission of  $t = 0.297 \pm 0.015$ .<sup>22</sup> Each particle traveling through the grid has a transmission probability  $t$  of making it to the detector. The DR events are now recorded at the full beam energy reduced by that percentage of the total mass of the fragments which are stopped by the grid. For  $\text{OPCl}^+$ , the separation of peaks in the pulse-height spectrum was just at resolution limit of the detector and could be used to provide a unique product determination, while in the case of  $\text{OPCl}_2^+$ , such a situation did not exist since the fragment peaks were below the noise level of the detector.

In order to address deficiencies in the literature, the thermochemical properties of  $\text{OPCl}_2^+$ ,  $\text{OPCl}^+$ , and  $\text{PCl}_2$  were calculated at the G3 level of theory<sup>23</sup> using GAUSSIAN03. The optimized structures were calculated at the MP2(Full)/6-31G(d) level as part of the G3 compound method. Wave function stability was verified at the HF/6-31G(d) level for all of the minimum energy structures, which is the initial optimization step of the G3 method. The G3 0 K energies and 298 K enthalpies are listed in Table I

TABLE I. Energies at 0 K and enthalpies at 298 K in hartrees calculated using G3 theory. The ionization potentials have been calculated using the G3 energies. The standard heats of formation at 298 K have been calculated using the atomization method. Literature values are given in parentheses. See text for details.

	Energy (0 K)	Enthalpy (298 K)	$\Delta H_f^{298}$ (kJ mol <sup>-1</sup> )	Ionization potential (eV)
$\text{OPCl}^+$	-876.080 906	-876.076452	827.9 (859 <sup>a</sup> )	
$\text{OPCl}$	-876.499 870 <sup>b</sup>	-876.495344 <sup>b</sup>	-269.5 (-274, <sup>c</sup> -251 <sup>d</sup> )	11.40 (11.5 <sup>d</sup> )
$\text{OPCl}_2^+$	1336.221 856	1336.216403	550.2	
$\text{OPCl}_2$	-1336.548 600 <sup>e</sup>	-1336.542990 <sup>e</sup>	-303.1	8.89
$\text{PCl}_2$	-1261.338 130	-1261.333342	-76.2	

<sup>a</sup>Experimental estimate (Ref. 25).

<sup>b</sup>G3 calculation (Ref. 8).

<sup>c</sup>Experimental estimate (Ref. 24).

<sup>d</sup>Experimental estimate (Ref. 26).

<sup>e</sup>G3 calculation (Ref. 7).

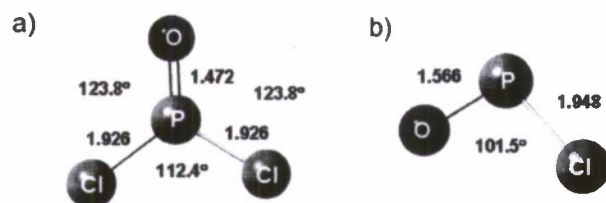


FIG. 3. Minimum energy structures for (a)  $\text{OPCl}_2^+$  and (b)  $\text{OPCl}^+$  optimized at the MP2(Full)/6-31G(d) level as part of G3 energy calculations.

for the three molecules just mentioned along with previous G3 calculations for  $\text{OPCl}_2$  and  $\text{OPCl}$  Refs. 7 and 8 as well as available experimental energetics for  $\text{OPCl}$  and  $\text{OPCl}^+$ .<sup>24–26</sup> Standard heats of formation at 298 K for the three species were calculated using the atomization method<sup>27</sup> and are also shown in Table I. Average absolute deviations of the enthalpies of formation calculated using G3 theory are  $+3.93 \text{ kJ mol}^{-1}$  ( $+0.94 \text{ kcal mol}^{-1}$ ).<sup>23</sup>

### III. RESULTS AND DISCUSSION

The optimized geometries obtained from the G3 calculations for  $\text{OPCl}_2^+$  and  $\text{OPCl}^+$  are shown in Figs. 3(a) and 3(b), respectively, having the energetics listed in Table I. The bond lengths and bond angles for neutral  $\text{PCl}_2$  and  $\text{OPCl}_2$  calculated by the MP2(Full)/6-31G(d) optimization step agree within  $0.005 \text{ Å}$  and  $0.5^\circ$ , respectively, with structures calculated by Miller *et al.*<sup>9</sup> using the bigger 6-311+G(d) basis set and are consequently not shown in Fig. 3. Similarly, the  $\text{OPCl}$  neutral structure has been calculated as part of previous G3 calculations.<sup>8</sup>  $\text{OPCl}_2^+$  is shown in Fig. 3(a) having a planar  $C_{2v}$  structure that is quite different from the nonplanar  $C_s$  structure of  $\text{OPCl}_2$ .<sup>9</sup> However, the P–O double bond in the cation has essentially the same length as in the neutral molecule,<sup>9</sup> while the P–Cl single bonds contract to around  $1.926 \text{ Å}$  in  $\text{OPCl}_2^+$ . In  $\text{OPCl}^+$ , the bond angle decreases by  $9^\circ$  from the neutral  $\text{OPCl}$ , while the P–Cl single bond contracts to  $1.948 \text{ Å}$  in the cation. The P–O bond in  $\text{OPCl}^+$  increases to an elongated double bond with length of  $1.566 \text{ Å}$ .

The standard heats of formation at 298 K and adiabatic ionization potentials (IP) of the neutrals calculated using G3 theory are also shown in Table I along with the available literature values. The neutral  $\text{OPCl}$  heat of formation found using G3 theory is  $-269.5 \text{ kJ mol}^{-1}$ , in agreement within the uncertainties of the experimental values of  $-274.15$  and  $-251.30 \text{ kJ mol}^{-1}$ .<sup>24,26</sup> The calculated IP of  $\text{OPCl}$  is  $11.40 \text{ eV}$ , in reasonable agreement with the  $11.5 \text{ eV}$  value estimated from electron impact experiments.<sup>25</sup> This estimated value has been used to determine the  $\text{OPCl}^+$  heat of formation to be  $859 \text{ kJ mol}^{-1}$ , which is over  $30 \text{ kJ mol}^{-1}$  higher than the G3 value. However, the estimated value agrees within the uncertainties of the experimental data used to determine it. Previous comparisons of G3 thermochemistry with the experimental values for  $\text{PO}_x\text{Cl}_y$  species have typically shown decent agreement.<sup>7,8,28,29</sup> Thus, the theoretical values given in Table I have been used to determine the energetics of the observed reaction channels.

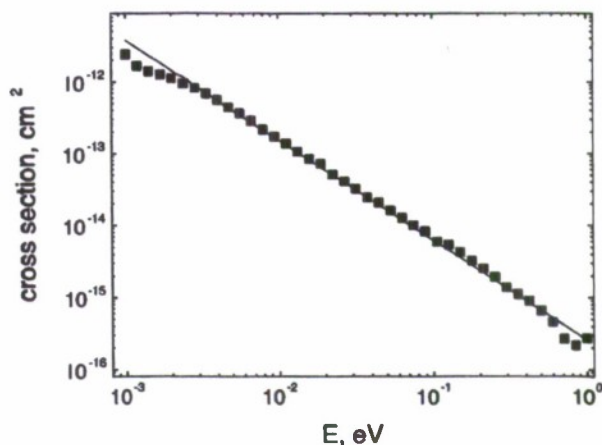


FIG. 4. Measured cross section for the DR of  $\text{OPCl}^+$  is presented by the solid squares. The line shows the best fit [Eq. (4)].

The derived cross section as a function of the interaction energy for the DR reaction of  $\text{OPCl}^+$  is shown in Fig. 4. Since cross sections for heavy polyatomic ions usually follow a power law  $\sigma_0/E^n$ , the best analytical description of the data presented in Fig. 4 is found to be

$$\sigma(E) = \frac{2.59 \times 10^{-16}}{E(\text{eV})^{1.39}} \text{ cm}^2. \quad (4)$$

The cross section is described by the same analytical expression over a wide range of interaction energies, which enables the thermal rate constant  $\alpha$  to be calculated analytically as a function of the electron temperature  $T_e$ ,

$$\alpha(T_e) = \sigma_0 e^n \sqrt{\frac{8}{\pi m_e}} \Gamma(2-n) (kT_e)^{1/2-n} \text{ cm}^3 \text{ s}^{-1}, \quad (5)$$

where  $\Gamma$  is the gamma function. Consequently, taking into account the loss factor of 16%, the reaction rate constant is derived to be

$$\alpha(T_e) = 7.63 \times 10^{-7} \left( \frac{T_e}{300} \right)^{-0.89} \text{ cm}^3 \text{ s}^{-1}. \quad (6)$$

As mentioned previously, the signal level for  $\text{OPCl}_2^+$  was close to the noise level of the detector (Fig. 2) which makes it impossible to determine the loss factor. Assuming that all of the DR products are detected, the derived cross section for the DR reaction of  $\text{OPCl}_2^+$  is shown in Fig. 5. However, the cathode voltage needed to match the velocity of the ion beam was extremely low,  $4.8 \text{ V}$ , and the bit errors in the DAC driving the cathode voltage give rise to instabilities in the voltage and therefore uncertainty in the electron energy. This is also the case for  $\text{OPCl}^+$  (the low energy part of Fig. 4 below  $3 \text{ meV}$ ), though to a much lesser extent due to the higher values of the cathode voltage. Consequently, the cross section for the DR of  $\text{OPCl}_2^+$  should be considered as being reliable only from  $0.006$  to  $0.3 \text{ eV}$ . The best fit over this interaction energy range was determined to be

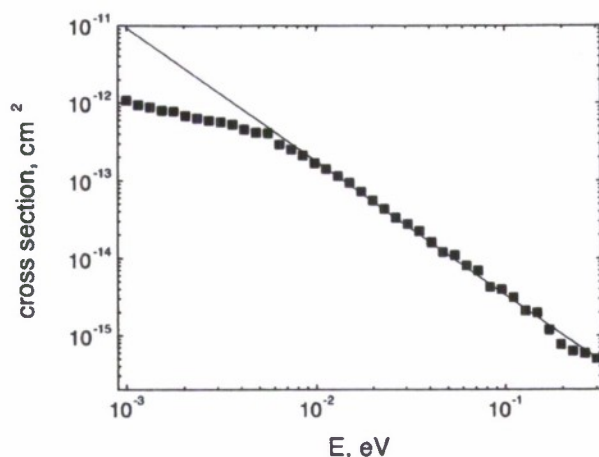


FIG. 5. The solid squares present the cross section for the DR of  $\text{OPCl}_2^+$ . The solid line is Eq. (7).

$$\sigma(E) = \frac{6.44 \times 10^{-17}}{E(\text{eV})^{1.72}} \text{ cm}^2. \quad (7)$$

Similarly, using Eq. (5) with the cross section presented in Eq. (7), the lower limit of the rate constant for the DR of  $\text{OPCl}_2^+$  is derived to be

$$\alpha(T_e) > 1.2 \times 10^{-6} \left( \frac{T_e}{300} \right)^{-1.22} \text{ cm}^3 \text{ s}^{-1}. \quad (8)$$

The systematic error in the rate constants for both  $\text{OPCl}^+$  and  $\text{OPCl}_2^+$ , which is dominated by the uncertainties in the interaction region length and the ion and electron currents, is estimated to be  $\approx 15\%$ .

The DR reaction usually proceeds through two competing processes called the direct and indirect mechanisms.<sup>30,31</sup> The direct mechanism involves the formation of a repulsive doubly electronically excited state, while the indirect mechanism proceeds through predissociative vibrationally excited Rydberg states on the neutral molecule. It is predicted that the energy dependence of the cross section of the purely direct process is  $1/E$  (Ref. 32) and, consequently, the temperature dependence of the rate constant must be  $1/T_e^{0.5}$  [Eq. (5)]. For the indirect mechanism, this dependence can be as steep as  $1/T_e^{1.5}$ .<sup>31</sup> The obtained temperature dependencies [Eqs. (6) and (8)] imply that the indirect mechanism plays a significant role in the DR reaction of both  $\text{OPCl}^+$  and  $\text{OPCl}_2^+$ . It is noted that the DR rate constants at 300 K for two other heavy triatomic molecular ions  $\text{O}_3^+$  and  $\text{N}_3^+$  are reported to be  $7.37 \times 10^{-7}$  and  $6.47 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ , respectively, values which are similar to those obtained here for  $\text{OPCl}^+$ .<sup>33,34</sup> The analysis for  $\text{OPCl}_2^+$  showed that the DR rate constant is  $> 1.2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  at an electron temperature of 300 K. Such large rate constants have previously been obtained for other ions containing heavy atoms:  $\text{DOCO}^+$ ,<sup>35</sup>  $\text{N}_2\text{OD}^+$ ,<sup>36</sup>  $\text{DCCCN}^+$ ,<sup>37</sup> and  $(\text{NO})_2^+$ .<sup>38</sup> The energy dependence reported here for  $\text{OPCl}_2^+$  is similar to that found for  $(\text{NO})_2^+$ .<sup>38</sup> The derived rate constants for both  $\text{OPCl}^+$  and  $\text{OPCl}_2^+$  indicate that the rate constant increases when the additional Cl atom is attached to  $\text{OPCl}^+$ . Such a tendency has previously been observed, in, e.g., oxygen and nitrogen com-

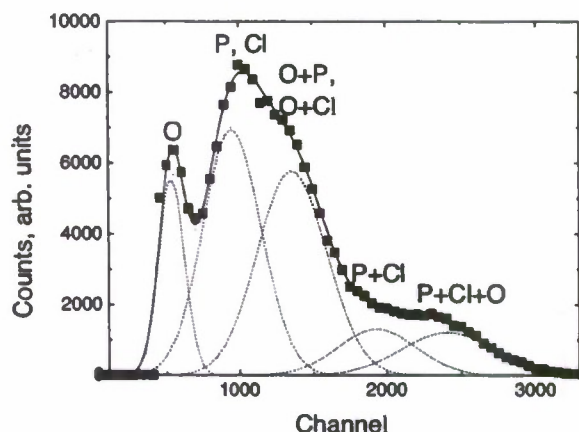


FIG. 6. Background-subtracted pulse-height spectrum for  $\text{OPCl}^+$  recorded at  $\approx 0$  eV interaction energy when the grid is inserted in front of the detector is shown by solid squares. The dotted curves present Gaussian curves of five peaks. The solid curve is an overall fitting.

pounds where the rate constants increase in the order  $\alpha(\text{X}_2^+) < \alpha(\text{X}_3^+) < \alpha(\text{X}_4^+)$  ( $\text{X}=\text{O}$  or  $\text{N}$ ).<sup>33,34,39–42</sup>

The background-subtracted pulse-height spectrum for  $\text{OPCl}^+$  with the grid inserted in front of the detector is shown in Fig. 6. The spectrum can be separated into five peaks (Fig. 6). Not every mass can be identified, e.g., the second peak corresponds to either a single P or Cl fragment hitting the detector. The branching fractions can be determined by solving a system of linear equations,

$$\begin{bmatrix} A(\text{O}) \\ A(\text{P, Cl}) \\ A(\text{O} + \text{P, O} + \text{Cl}) \\ A(\text{P} + \text{Cl}) \\ A(\text{P} + \text{Cl} + \text{O}) \end{bmatrix} = \begin{bmatrix} t(1-t)^2 & t(1-t) & 0 & 0 \\ 2t(1-t)^2 & 0 & t(1-t) & t(1-t) \\ 2t^2(1-t) & 0 & t(1-t) & t(1-t) \\ t^2(1-t) & t(1-t) & 0 & 0 \\ t^3 & t^2 & t^2 & t^2 \end{bmatrix} \times \begin{bmatrix} N_a \\ N_b \\ N_c \\ N_d \end{bmatrix}, \quad (9)$$

where  $N_a$ ,  $N_b$ ,  $N_c$ , and  $N_d$  represent the branching fractions of the (1a)–(1d) channels,  $A$  is the number of counts in the peak, and  $t$  is the transmission of the grid. It is noted that the third and the fourth columns in the probability matrix are the same, which means that it is not possible to derive the fractions of the (1c) and (1d) channels separately and, therefore, only their sum can be calculated. In order to determine the branching fractions of all the channels either the P and Cl peaks, or, P+O and Cl+O peaks would need to be resolved, something which is not possible with the current detector. Instead, we rely on chemical intuition based on the limited amount of data available on DR studies involving triatomic systems with only heavy atoms. It is unlikely that during the short time period during which recombination takes place that the heavy outside atoms can combine. The three studied systems confirm the absence of rearrangement, i.e.,  $\text{O}_2$  formation from the DR of both  $\text{SO}_2^+$  and  $\text{CO}_2^+$  as well as pro-

duction of OS from the DR of  $\text{OCS}^+$  have been found to be vanishingly small.<sup>43–45</sup> Based on these observations, (1d) channel is assumed to be negligible. Finally, the branching fractions were derived to be  $N_a = 0.16 \pm 0.07$ ,  $N_b = 0.16 \pm 0.03$ ,  $N_c = 0.68 \pm 0.05$ , and  $N_d = 0$ .

Of the two channels that produce diatomic neutrals, the more exothermic channel is more abundant. This result might be expected since the P–Cl and O–P bond lengths are 1.95 and 1.57 Å, respectively [Fig. 3(b)]. The likelihood of the bond rupture in the DR reaction seems to depend on the bond strength, i.e., the cleavage of the weaker bond is more likely. The branching fraction for the three-body channel is 16% which is comparable to that of single O–P bond rupture. The efficiency at which the DR reaction breaks multiple covalent bonds in light polyatomic molecular ions, especially of the type  $\text{XH}_2^+$  where  $X = \text{H, D, O, C, N, P}$ , etc., is well known,<sup>14–16,46</sup> and such reactivity has also been observed in heavy triatomic ions. Of particular interest here, it has been found that the DR of  $\text{N}_3^+$  and  $\text{O}_3^+$  ions gives rise to almost completely opposite branching behavior, with 94% of ozone molecules breaking both bonds in the reaction while only 8% of azide molecules manage this.<sup>33,34</sup> Furthermore, the full fragmentation channels in the DR reaction of  $\text{SO}_2^+$  and  $\text{N}_2\text{O}^+$  are 39 and 16%, respectively.<sup>44,47</sup> Due to the sparse amount of available information, so far it is hard to find similarities in the breakup dynamics of the heavier triatomic ions.

#### IV. CONCLUSIONS

The present studies test the high mass capability at CRYRING for investigating the DR reaction. For  $\text{OPCl}^+$ , with a mass of 84 amu, due to a combination of the slowness of the ions and the poor phase-space cooling  $\approx 16\%$  of the DR products missed the detector. Nevertheless, this missing fraction is accounted for in the analysis and did not present a serious problem. However, for  $\text{OPCl}_2^+$  (mass 117 amu) which has an even lower kinetic energy, such losses represented a significantly greater problem, and in order to make some of the measurements feasible, a larger detector was used. Although the higher electrical noise generated in this detector did not allow the amount of losses to be estimated, analysis of those particles which were detected allowed a lower limit of the rate constant to be determined. The relatively high value of the derived reaction rate constant is similar to those obtained for other molecular ions of a similar size which could indicate that the majority of the DR products were detected. It is not clear whether spending large amounts of time focusing the ions could alleviate the beam spread issue though, in practical terms, it is complicated by the fact that the electron cooling time is much longer than the lifetime of the ions in the ring. The relative effectiveness of spending such a long time cooling the beam also depends on the amount of ions, since there have to be a sufficient number remaining to make a measurement feasible. For the very heavy ions discussed here,  $\text{OPCl}^+$  and  $\text{OPCl}_2^+$ , such ion currents were not feasible and so cooling for the required length of time would have been impossible. Additional constraints on the reliability of the data may also arise from the low kinetic energy of the electrons needed to match the ion beam

velocity for near 0 eV relative collision energies. In determining the product distributions from the DR reaction, these measurements also push the limit of what is possible. For  $\text{OPCl}_2^+$  it was not possible to derive any product information at all. Even for  $\text{OPCl}^+$ , where the smallest mass difference between products is 6 amu, the signals these masses generated in the detector blended together, and only a Gaussian analysis of the peaks combined with the loss measurements and previously observed chemical precedents for the absence of rearrangement in heavy ions in DR allowed for a complete branching determination to be made.

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